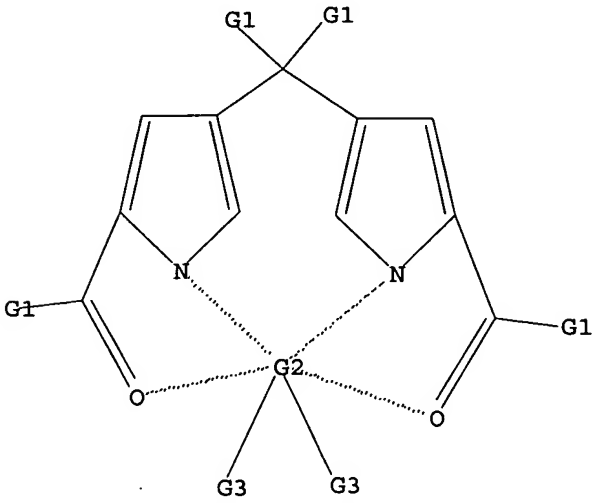
10/654,181

(FILE 'HOME' ENTERED AT 15:02:58 ON 26 MAR 2005)

FILE 'REGISTRY' ENTERED AT 15:03:10 ON 26 MAR 2005
L1 STRUCTURE UPLOADED

=> d l1
L1 HAS NO ANSWERS
L1 STR



G1 H,Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,Ph

G2 Si,Ge,Pb,Sn

G3 Cb,Ak

Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 15:04:05 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 31 TO ITERATE

100.0% PROCESSED 31 ITERATIONS 0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 286 TO 954
PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 15:04:11 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 785 TO ITERATE

100.0% PROCESSED 785 ITERATIONS 0 ANSWERS
SEARCH TIME: 00.00.01

L3 0 SEA SSS FUL L1

=> fil caplus
COST IN U.S. DOLLARS SINCE FILE ENTRY 161.76 TOTAL SESSION 161.97

FULL ESTIMATED COST

FILE 'CAPLUS' ENTERED AT 15:04:38 ON 26 MAR 2005

FILE COVERS 1907 - 26 Mar 2005 VOL 142 ISS 14
FILE LAST UPDATED: 25 Mar 2005 (20050325/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

```
=> s "1,9-diacyldipyrromethane"
       8217170 "1"
       1740088 "9"
             7 "DIACYLDIPYRROMETHANE"
L4           6 "1,9-DIACYLDIPYRROMETHANE"
                ("1"(W)"9"(W)"DIACYLDIPYRROMETHANE")

=> d 1-6 bib abs
```

L4 ANSWER 1 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2005:220204 CAPLUS
TI Facile synthesis of 1,9-diacyldipyrromethanes
IN Lindsey, Jonathan S.; Tamaru, Shunichi; Yu, Lianhe
PA USA
SO U.S. Pat. Appl. Publ., 23 pp.
CODEN: USXXCO
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 2005054858	A1	20050310	US 2003-654181	20030903
PRAI US 2003-654181		20030903		

AB The present invention provides a method of making a metal complex. The method comprises the steps of: (a) acylating a dipyrromethane or a 1-monoacyldipyrromethane to form a mixed reaction product comprising a 1,9-diacyidipyrromethane; (b) combining the reaction product with a compound of the formula R 2 MX 2 in the presence of a base, where R is alkyl or aryl, M is Sn, Si, Ge, or Pb (preferably Sn), and X is halo, OAc, acac, or OTf, to form a product comprising a metal complex of the formula DMR 2 in the mixed reaction product, wherein D is a **1,9-diacyldipyrromethane**; and then (c) separating the metal complex from the mixed reaction product. The method may be utilized for the convenient synthesis and separation of 1,9-diacyldipyrromethanes. Metal complex intermediates useful in such methods are also described.

L4 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2005:192542 CAPLUS
TI Facile synthesis and purification of 1,9-diacyldipyrromethanes
AU Zaidi, Syeda Huma H.; Kannan, Muthukumaran; Lindsey, Jonathan S.
CS Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA
SO Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005 (2005), ORGN-522 Publisher: American Chemical Society, Washington, D. C.
CODEN: 69GQMP
DT Conference; Meeting Abstract
LA English
AB 1,9-Diacyldipyrromethanes are important precursors to porphyrins, yet synthetic access remains limited owing to (1) poor conversion in the

9-acylation of 1-acyldipyrromethanes, and (2) handling difficulties because acyldipyrromethanes typically streak upon chromatog. and give amorphous powders upon attempted crystallization thereby requiring lengthy chromatog. for purification We have developed methodol. that sidesteps such handling problems by employing the 1-acyldipyrromethane-BR2 complex 1 as a substrate for 9-acylation. The dialkylboron unit provides protection for the α-acylpyrrole unit. 9-Acylation requires formation of the pyrrolyl-MgBr reagent and the presence of one equiv of a non-nucleophilic base to quench the proton liberated upon α-acylation. The acylation method affords **1,9-diacyldipyrromethane**-BR2 complexes 2 with limited or no chromatog. in excellent yields.

L4 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2004:930110 CAPLUS
DN 142:93562
TI 9-Acylation of 1-Acyldipyrromethanes Containing a Dialkylboron Mask for the α-Acylpyrrole Motif
AU Zaidi, Syeda Huma H.; Muthukumaran, Kannan; Tamaru, Shun-ichi; Lindsey, Jonathan S.
CS Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA
SO Journal of Organic Chemistry (2004), 69(24), 8356-8365
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
AB 1,9-Diacyldipyrromethanes are important precursors to porphyrins, yet synthetic access remains limited owing to (1) poor conversion in the 9-acylation of 1-acyldipyrromethanes and (2) handling difficulties because acyldipyrromethanes typically streak upon chromatog. and give amorphous powders upon attempted crystallization A reliable means for converting a dipyrromethane to a 1-acyldipyrromethane-dialkylboron complex was recently developed, where the dialkylboron (BR2) unit renders the complex hydrophobic and thereby facilitates isolation. Herein a refined preparation of 1,9-diacyldipyrromethanes is presented that employs the 1-acyldipyrromethane-BR2 complex as a substrate for 9-acylation. The dialkylboron unit provides protection for the α-acylpyrrole unit. 9-Acylation requires formation of the pyrrolyl-MgBr reagent and the presence of 1 equiv of a nonnucleophilic base to quench the proton liberated upon α-acylation. Reaction of the 1-acyldipyrromethane-BR2 complex (1 equiv) with mesitylmagnesium bromide (2 equiv) followed by the addition of an acylating agent (S-2-pyridyl thioate or acid chloride, 1.1 equiv) gives the corresponding **1,9-diacyldipyrromethane**-BR2 complex. The acylation method afforded **1,9-diacyldipyrromethane**-BR2 complexes with limited or no chromatog. in yields of 64-92%. The **1,9-diacyldipyrromethane**-BR2 complexes are stable to routine handling, are readily soluble in common organic solvents, crystallize readily, and can now be prepared in multigram quantities through use of stoichiometric quantities of reagents.
RE.CNT 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 4 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2004:45741 CAPLUS
DN 140:217731
TI A Tin-Complexation Strategy for Use with Diverse Acylation Methods in the Preparation of 1,9-Diacyldipyrromethanes
AU Tamaru, Shun-ichi; Yu, Lianhe; Youngblood, W. Justin; Muthukumaran, Kannan; Taniguchi, Masahiko; Lindsey, Jonathan S.
CS Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA
SO Journal of Organic Chemistry (2004), 69(3), 765-777
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
AB The acylation of dipyrromethanes to form 1,9-diacyldipyrromethanes is an essential step in the rational synthesis of porphyrins. Although several

methods for acylation are available, purification is difficult because 1,9-diacyldipyrromethanes typically streak extensively upon chromatog. and give amorphous powders upon attempted crystallization A solution to this problem has been achieved by reacting the **1,9-diacyldipyrromethane** with Bu2SnCl2 to give the corresponding dibutyl(5,10-dihydrodipyrrinato)tin(IV) complex. The reaction is selective for dipyrromethanes that bear acyl groups at both the 1- and 9-positions but otherwise is quite tolerant of diverse substituents. The diacyldipyrromethane-tin complexes are stable to air and water, are highly soluble in common organic solvents, crystallize readily, and chromatograph without streaking. Four methods (Friedel-Crafts, Grignard, Vilsmeier, benzoxathiolium salt) were examined for the direct 1,9-diacylation of a dipyrromethane or the 9-acylation of a 1-acyldipyrromethane. In each case, treatment of the crude reaction mixture with Bu2SnCl2 and TEA at room temperature enabled facile isolation of multigram quantities of the **1,9-diacyldipyrromethane**-tin complex. The diacyldipyrromethane-tin complexes could be decomplexed with TFA in nearly quant. yield. Alternatively, use of a diacyldipyrromethane-tin complex in a porphyrin-forming reaction (reduction with NaBH4, acid-catalyzed condensation with a dipyrromethane, DDQ oxidation) afforded the desired free base porphyrin in yield comparable to that obtained from the uncomplexed diacyldipyrromethane. The acylation/tin-complexation strategy has been applied to a bis(dipyrromethane) and a porphyrin-dipyrromethane. In summary, the tin-complexation strategy has broad scope, is compatible with diverse acylation methods, and greatly facilitates access to 1,9-diacyldipyrromethanes.

RE.CNT 57 THERE ARE 57 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 2003:635458 CAPLUS
TI Refined synthesis of **1,9-diacyldipyrromethane**
AU Tamaru, Shun-ichi; Youngblood, Justin; Muthukumaran, Kannan; Yu, Lianhe; Lindsey, Jonathan S.
CS Department of Chemistry, North Carolina State University, Raleigh, NC, 27696-8204, USA
SO Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), ORGN-371 Publisher: American Chemical Society, Washington, D. C.
CODEN: 69EKY9
DT Conference; Meeting Abstract
LA English
AB Meso-substituted porphyrins bearing specific patterns of functional groups are valuable components in the synthesis of porphyrin-based biomimetic systems and mol. materials. Dipyrromethanes bearing acyl groups at the 1- and 9-positions are key precursors to such porphyrins. Dipyrromethanes bearing identical groups at the 1- and 9-positions enable synthesis of trans-AB2C-porphyrins, while those with different groups enable the synthesis of porphyrins bearing four different substituents (ABCD-porphyrins). Two distinct methods for diacylation with identical acyl species include (1) treatment with EtMgBr followed by an acid chloride, or (2) alkylation with a 2-aryl-1,3-benzoxathiolium tetrafluoroborate followed by oxidative hydrolysis. Both methods require chromatog. to sep. the diacyl and monoacyl dipyrromethanes. We have developed improved acylation chemical and separation methodol. that facilitate synthesis and isolation of 1,9-diacyldipyrromethanes.

L4 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1995:898533 CAPLUS
DN 124:29488
TI Synthetic approaches to regioisomerically pure porphyrins bearing four different meso-substituents
AU Lee, Chang-Hee; Li, Feirong; Iwamoto, Koji; Dadok, Josef; Bothner-By, Aksel A.; Lindsey, Jonathan S.
CS Dep. Chemistry, Carnegie Mellon Univ., Pittsburgh, PA, 15213, USA
SO Tetrahedron (1995), 51(43), 11645-72
CODEN: TETRAB; ISSN: 0040-4020
PB Elsevier
DT Journal

LA English
OS CASREACT 124:29488
AB Regioisomerically pure porphyrins bearing four different meso-substituents have been synthesized via a 9-step route starting from pyrrole and carbonyl-containing compds. This synthesis builds on a one-flask synthesis of 1,9-unsubstituted dipyrromethanes. An acyl group is introduced selectively in the 1-position of the dipyrromethane by use of an acid chloride and the dipyrromethane Grignard reagent, which resembles the pyrrole Grignard reagent. In contrast to the 2- and 5-positions of a monomeric pyrrole, the 1- and 9-positions of a dipyrromethane are relatively non-interacting and can be functionalized independently. A 2-aryl-1,3-benzoxanthiolium tetrafluoroborate, available from carbonyl containing compds., serves as a latent acyl equivalent and alkylates regiospecifically the 9-position of a 1-acyldipyrromethane. Alternatively the 1- and 9-positions of a dipyrromethane can be functionalized independently by successive alkylations with two different 2-aryl-1,3-benzoxanthiolium tetrafluoroborates. Hydrolysis of the mono or di(benzoxathiolyl)dipyrromethane followed by reduction of the **1, 9-diacyldipyrromethane** affords the corresponding dipyrromethanediol. An acid-catalyzed MacDonald-type 2 + 2 condensation of the dipyrromethanediol and a 1,9-unsubstituted dipyrromethane at room temperature followed by oxidation with DDQ gives the porphyrin bearing four different meso-substituents. The reaction sequence resulted in a single porphyrin isomer without acidolytic scrambling of the four meso-substituents. The porphyrin structures were confirmed by laser desorption mass spectrometry and by high field high resolution proton NMR spectroscopy. An entire synthesis can be performed in about two weeks. The controlled stepwise synthesis of porphyrins bearing four different meso-substituents should enable preparation of multi-functionalized porphyrin building blocks for application in the synthesis of bioorg. model systems.